SOLIDIFICATION

METE 327, Fall 2008

OUTLINE

- The Liquid Phase
- Nucleation
- Crystal Growth, Solid-Liquid Interface
- Dendritic Growth
- Freezing in Alloys
- Freezing of Ingots
- Eutectic Freezing
- Metallic Glass

SOLIDIFICATION

Why do we need to know about solidification?

Many metal components are formed as castings

The primary initial form for wrought alloys is the cast ingot

Welding processes involve solidification phenomena

Alloy powders are often atomized, and rapidly solidified

Metastable microstructures, phases and glasses are becoming more widely used.

What is the liquid phase?

We know a great deal about ordering and atomic arrangements in the solid phase because of information from x-ray, electron, neutron diffraction and TEM observations.

The gas phase is at the opposite extreme, with little or no interaction between atoms, complete randomness, and disorder.

There is no simple picture of the liquid phase.

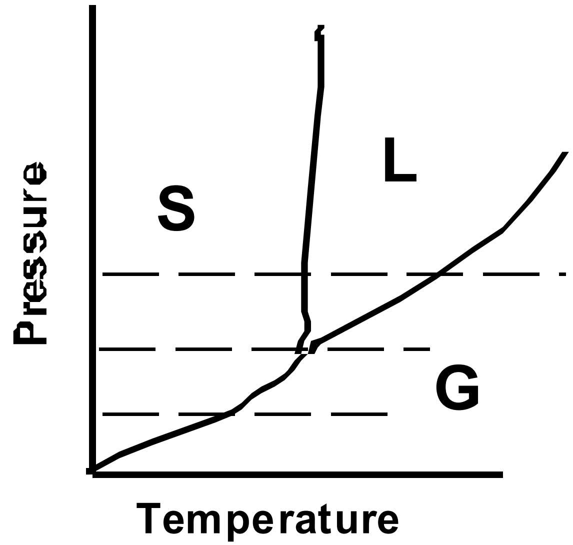
*The average separation of atoms is close to that found in solid. (The change in density on melting of metals is about 2-6%)

*The latent heat of fusion is 1/25 to 1/40 of the latent heat of vaporization.

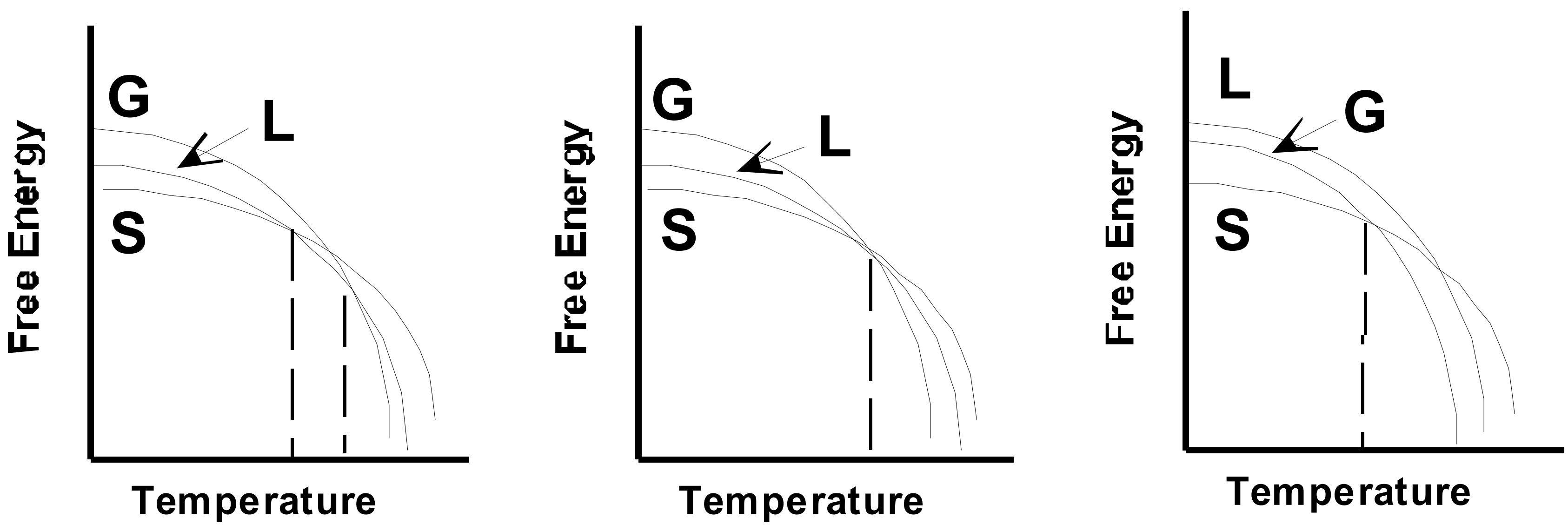
*X-ray diffraction shows about the same coordination of atoms as in the solid. There is short range order, but no long range order.

*Diffusion rates are several orders of magnitude greater than in the solid state, meaning that there are smaller energy barriers for atom movement.

*Most liquid metals have similar properties, while their solids do not.



Single component phase diagram with isobars, and related free energy plots



NUCLEATION

The solidification of metals occurs by nucleation and growth.

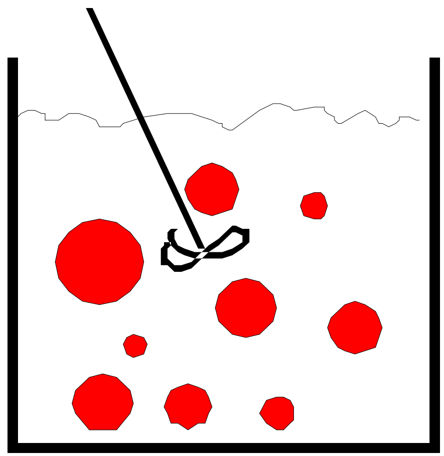
The same is true of melting (maybe) but the barriers are much less.

Thus, it is possible to achieve significant supercooling of pure metal liquids.

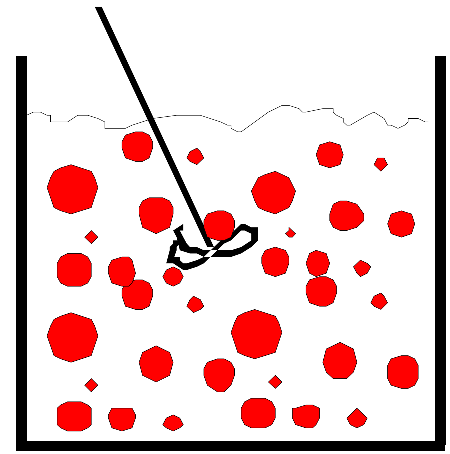
Undercooling or supercooling is achieved by suppressing heterogeneous nucleation. “Prenucleants” are assumed to exist in the liquid metal. In many processes, homogeneous nucleation is assumed to occur, but experimental evidence suggests otherwise.

What is the evidence?

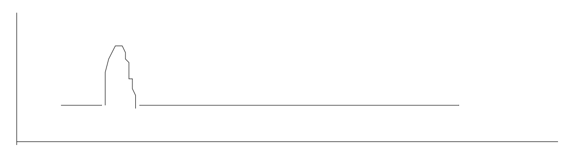
The Experiments of Perepezko



Before stirring



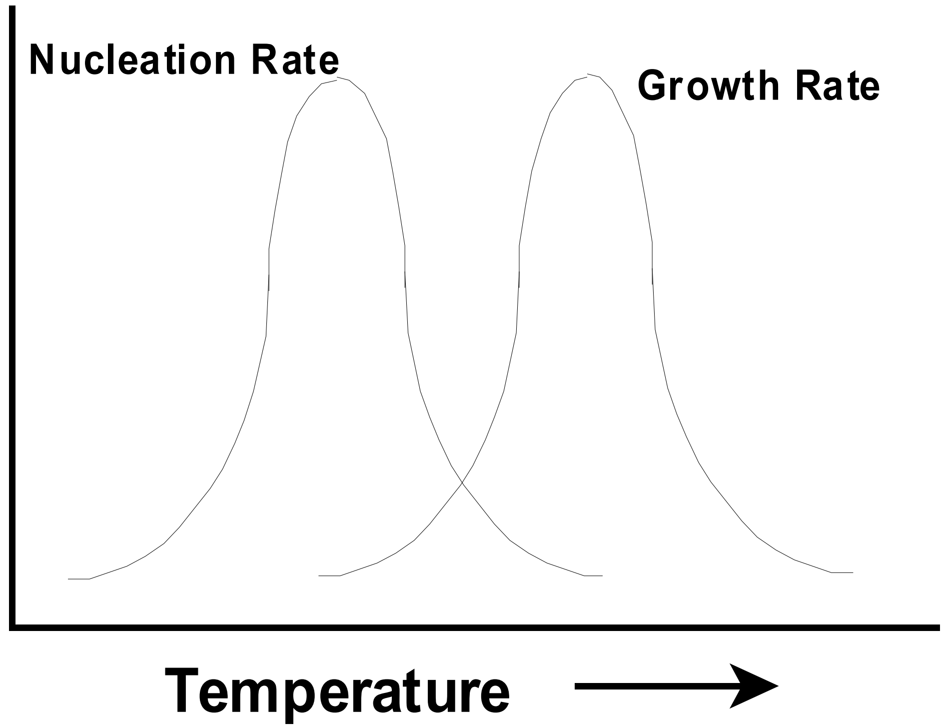
After stirring



An emulsion is made with the metal dispersed in a molten salt. When the emulsion makes much finer droplets, more undercooling can be achieved before the evidence of freezing is noted.

Metal Max undercooling, K

Hg	88
Cd	110
Pb	153
Al	160
Sn	187
Ag	227
Au	230
Cu	236
Fe	286
Mn	308
Ni	365
Pt	370
Nb	525

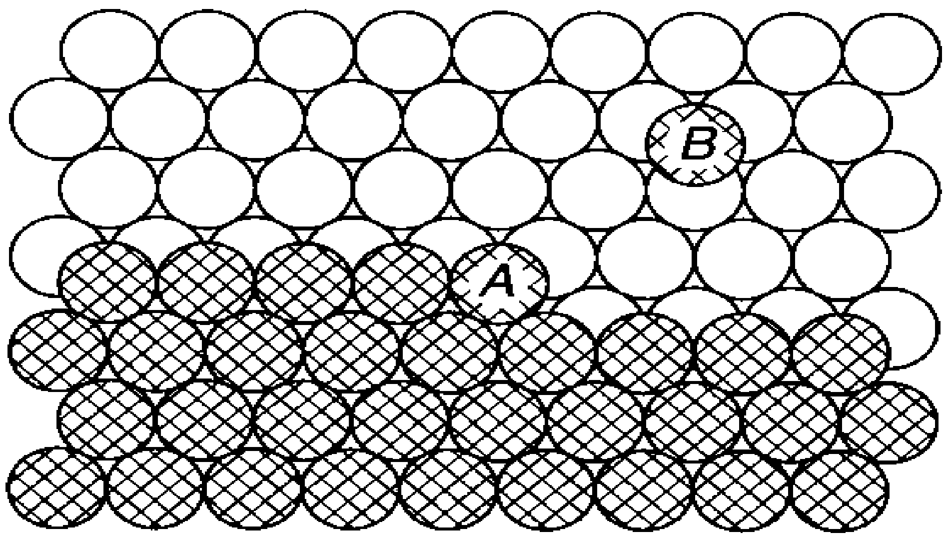


Nucleation is fastest at lower temperature

Figure 14.4 in text shows undercooling for a complete range of Cu-Ni alloys

Crystal Growth from the Liquid Phase:

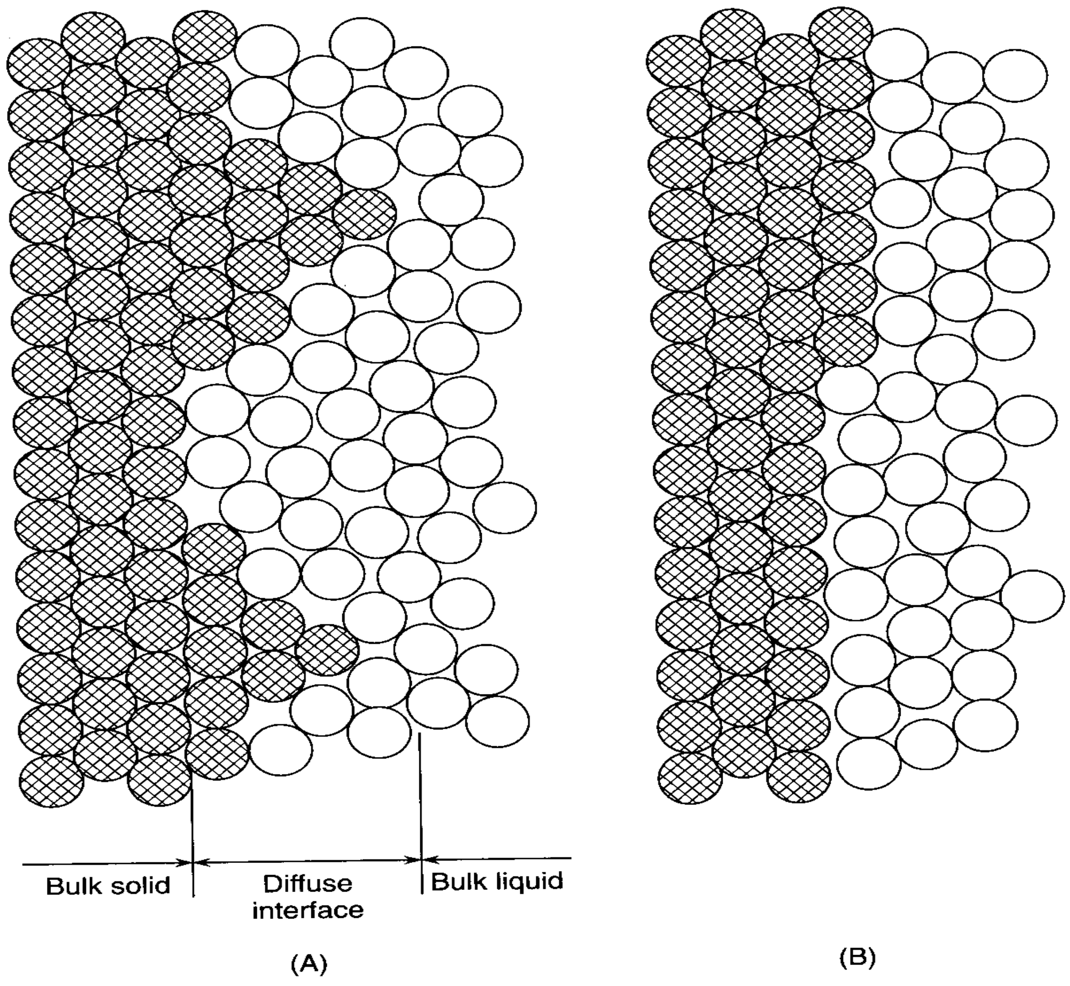
The movement of a boundary separating liquid from solid, under the influence of a temperature gradient normal to the boundary, is the result of two different atomic movements.



Atoms leave the liquid and join the solid = rate of attachment
Atoms leave the solid and join the liquid = rate of detachment

Nature of the Solid-Liquid Interface:

Usually we consider only the two extreme cases, as illustrated below:



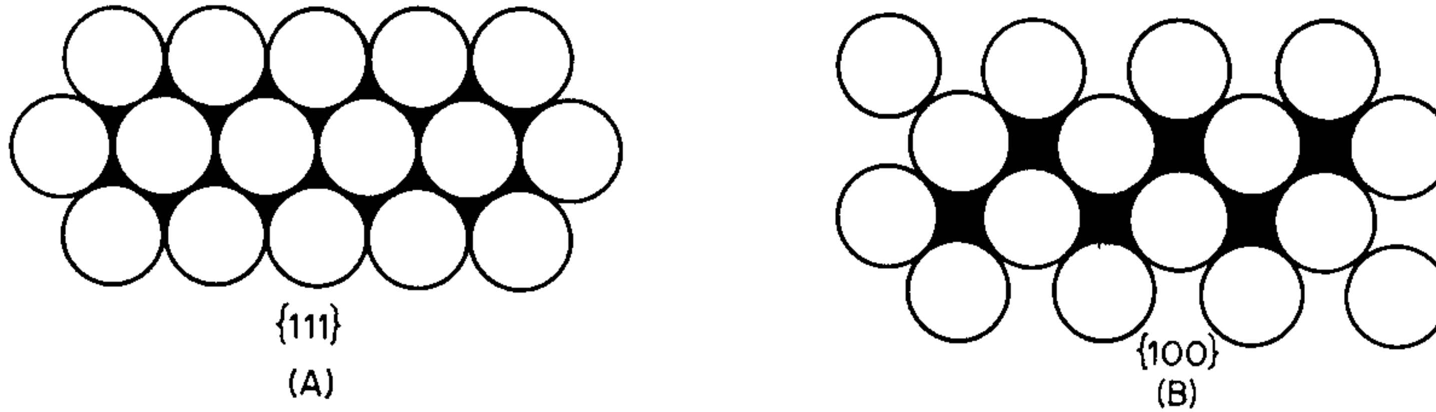


Fig. 14.14 Planes of looser packing, such as {100}, are better able to accommodate an atom that leaves the liquid to join the solid than a closer packed plane, such as {111}. Illustrated planes correspond to a face-centered cubic lattice. (After Chalmers, B., *Trans. AIME*, **200** 519 [1954].)

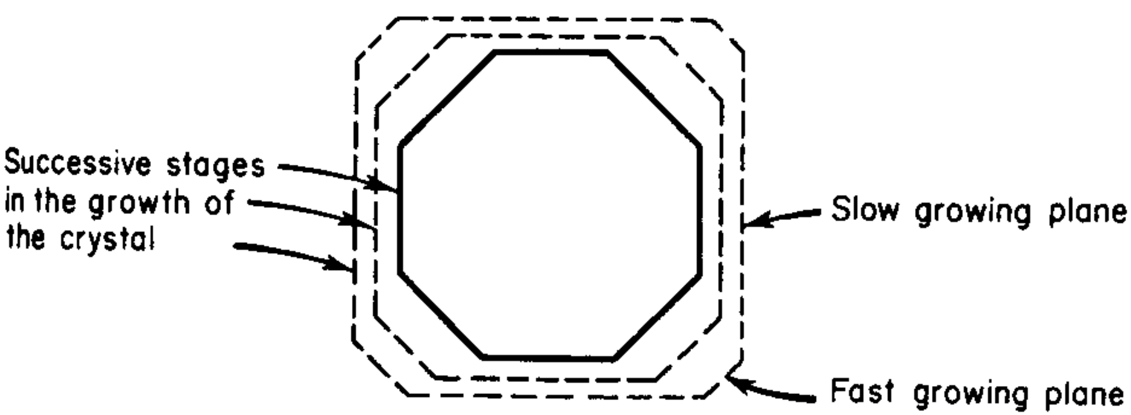


Fig. 14.15 A crystal growing in a liquid tends to develop faces that are slow-growing (close-packed).

Planes of looser atomic packing can better accommodate an atom that leaves the liquid.

A growing crystal will assume faces that represent slow growing planes.

The rate of movement of a solid-liquid interface varies linearly with the amount of undercooling at the interface.

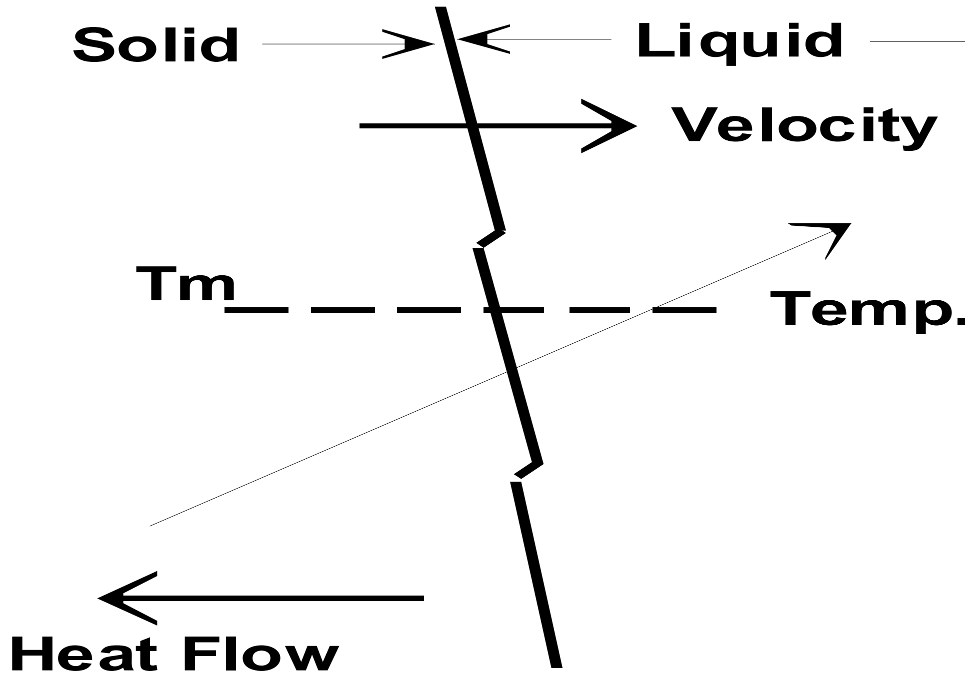
The velocity, V, is related to the net frequency of atoms joining the solid, since atoms are continuously leaving or joining the interface.

A simplified relation is:

$$V = B\Delta T$$

Stable Interface Freezing:

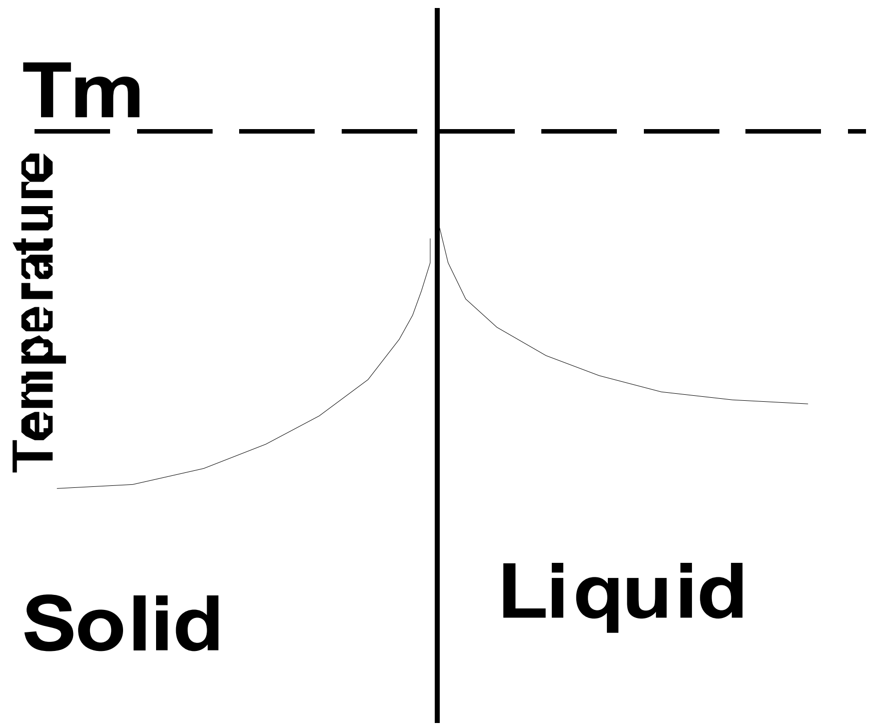
Removal of the heat of fusion from the interface–if there is a thermal gradient perpendicular to the interface, increasing into the liquid, a stable planar interface can move forward as a unit. This also depends on undercooling.



A sketch of the moving solid-liquid interface where the temperature gradient is high, the velocity is also high, and the heat flow is sufficient to remove the latent heat of solidification.

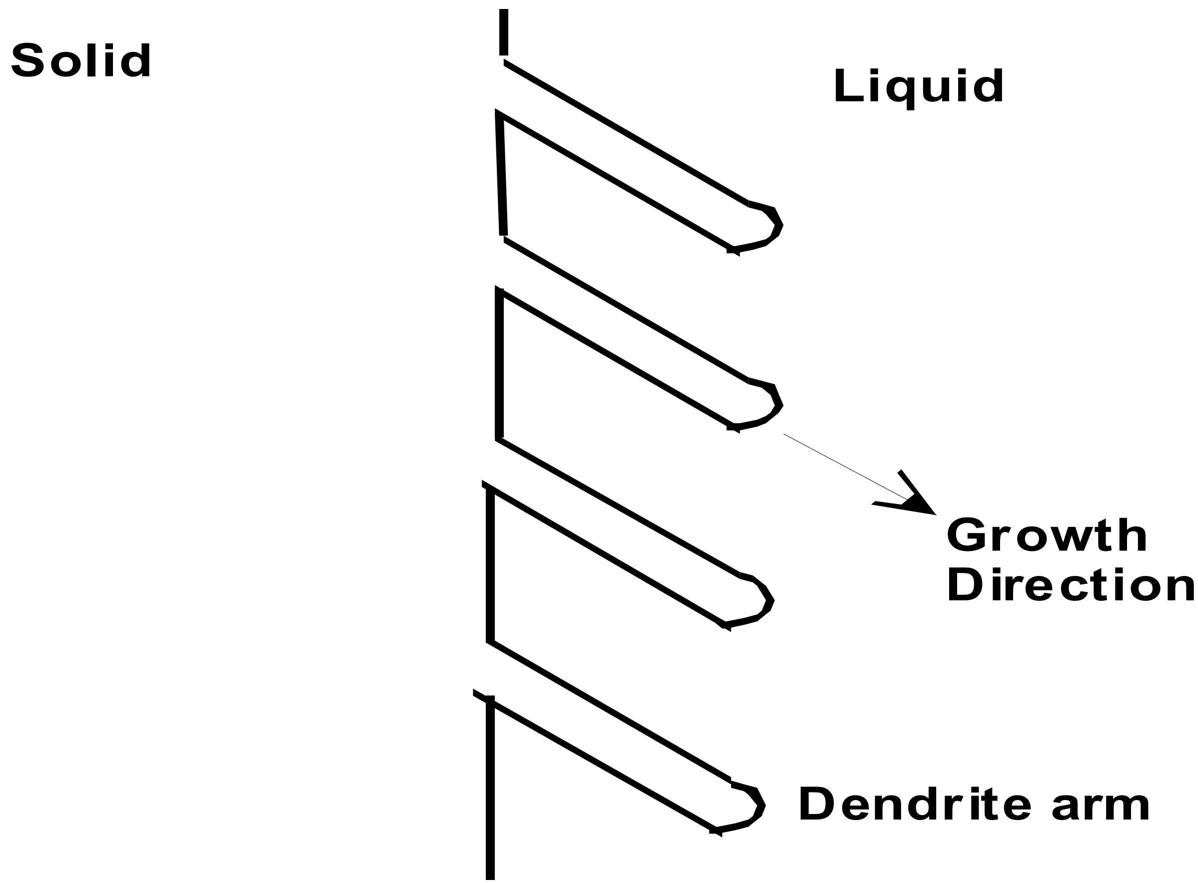
DENDRITIC GROWTH

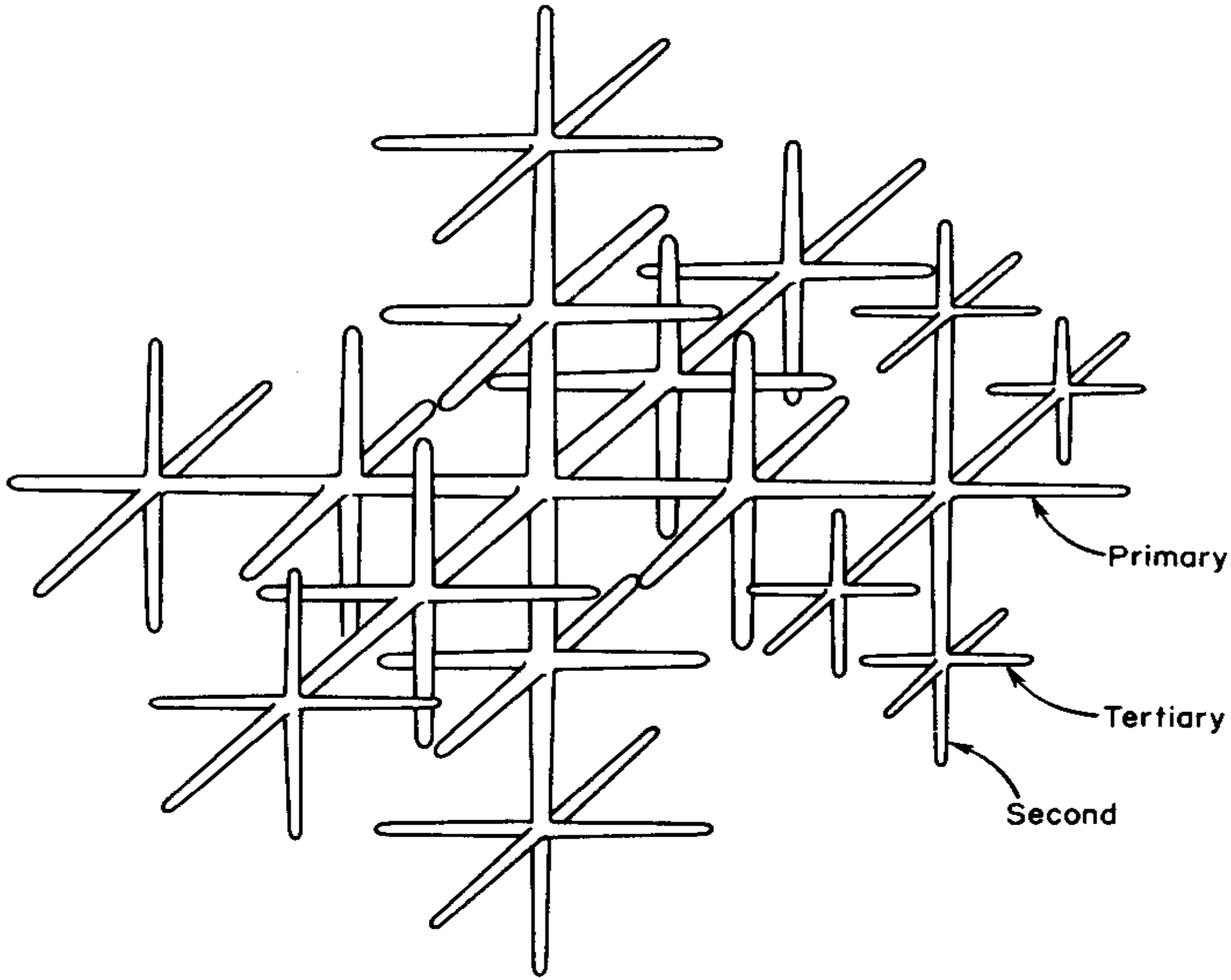
Pure Metals:



This represents a temperature inversion during freezing. The temperature decreases into the liquid, ahead of the solid-liquid interface.

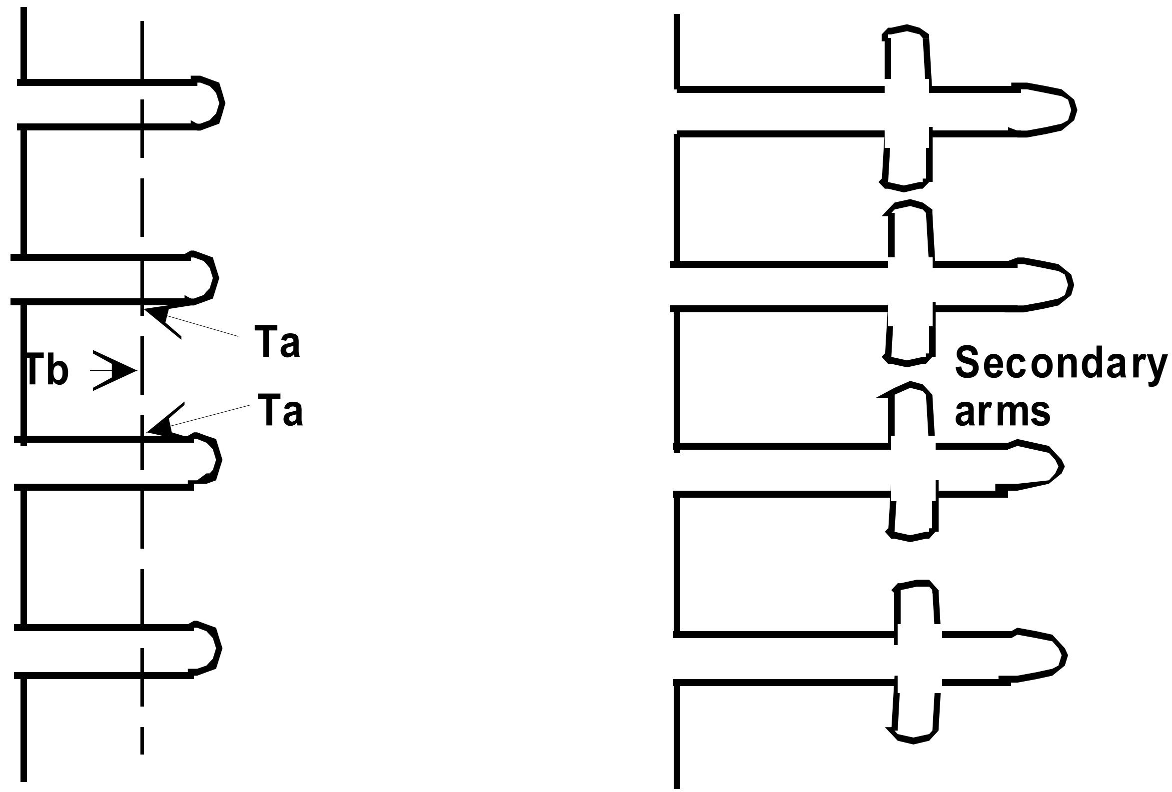
The first stage of dendritic growth





Dendritic growth can be quite complicated!

How do such complicated structures arise?



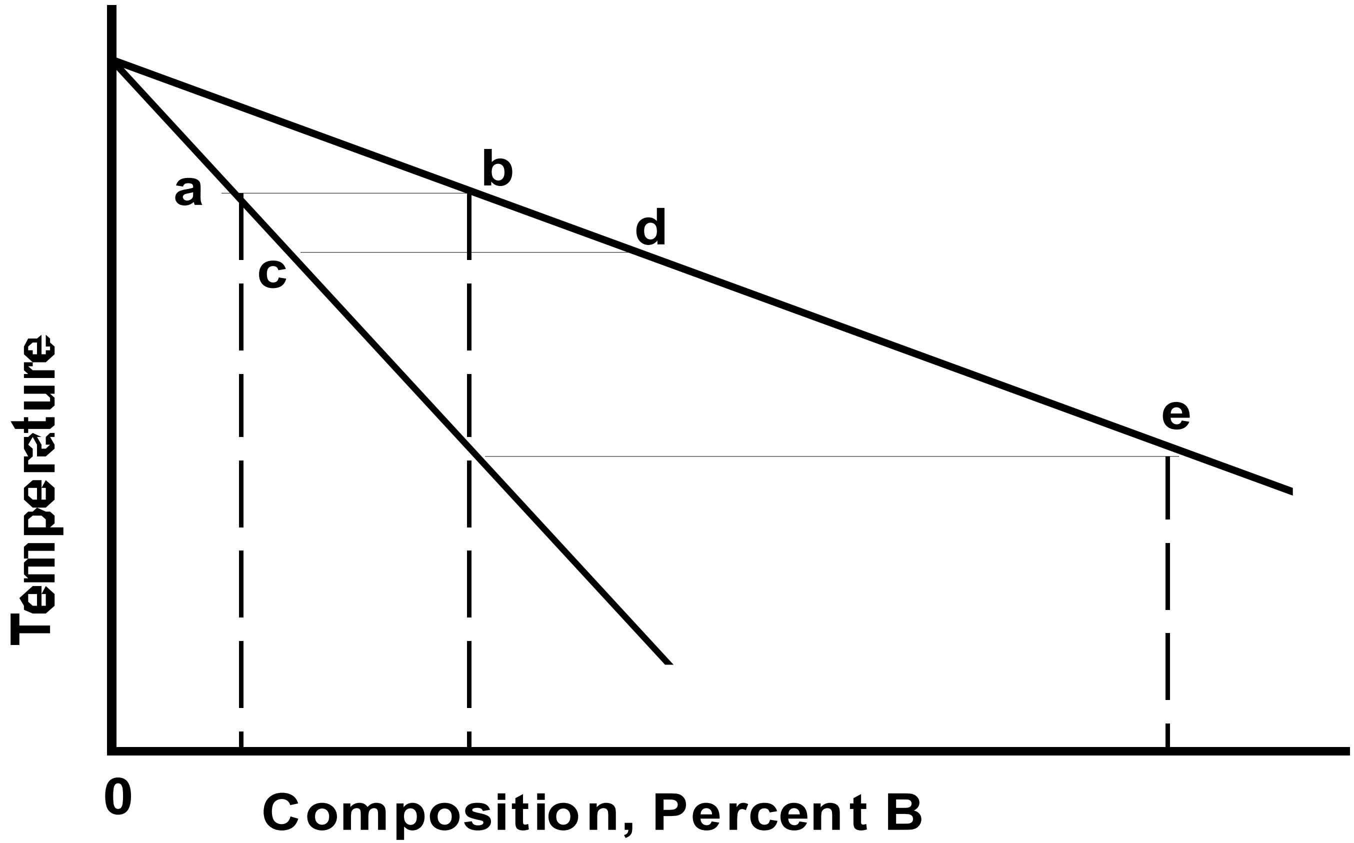
Secondary arms arise because there is a falling temperature gradient between arms such that Ta > Tb

Dendritic Growth Directions in Various Crystal Structures

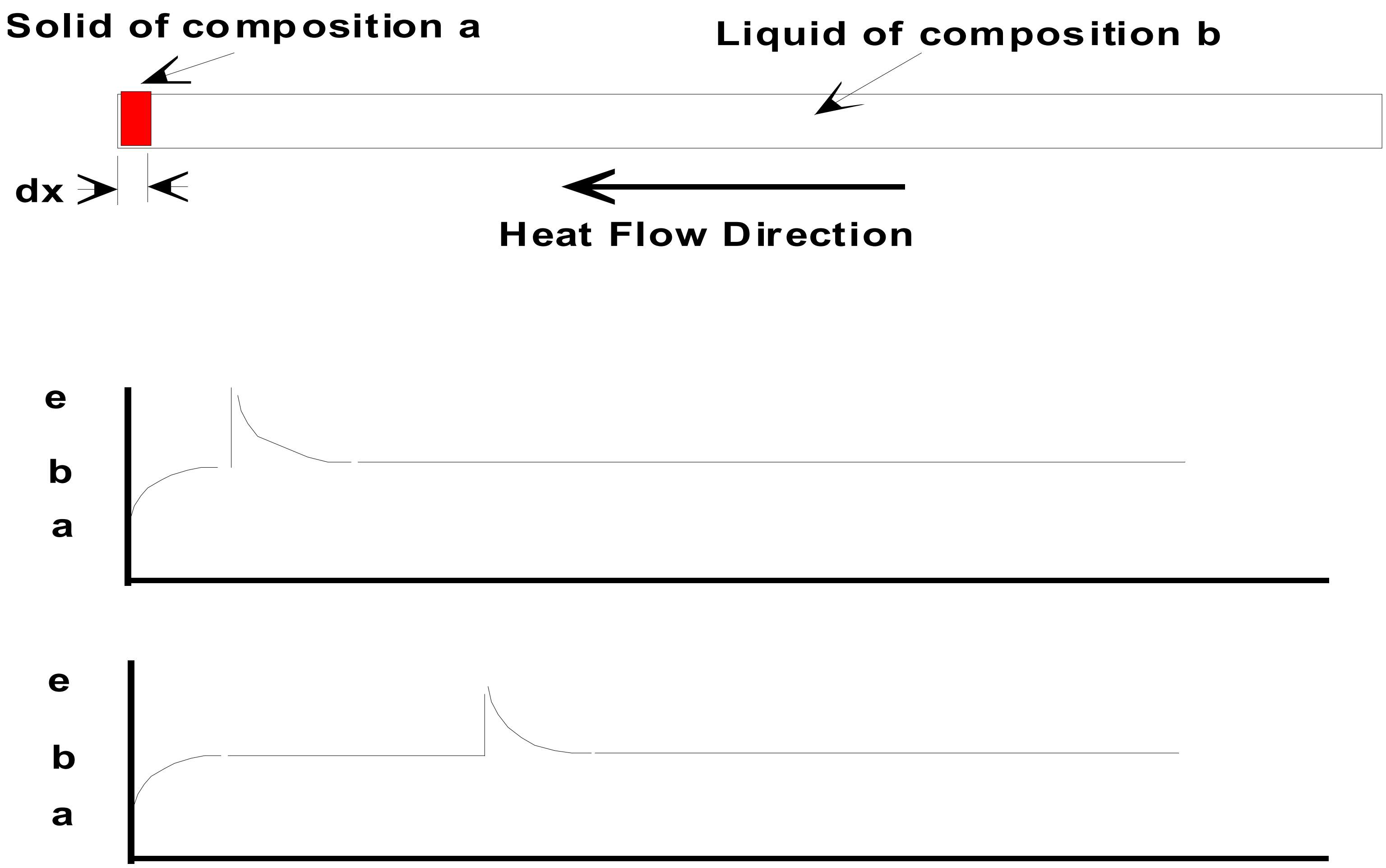
FCC	<100>
BCC	<100>
HCP	<10-10>
BCT (tin)	<110>

In cubic crystals the <100> dendrite arm growth direction leads to the secondary arms being perpendicular to the primary arms. Also, the tertiary arms are perpendicular to the secondary arms.

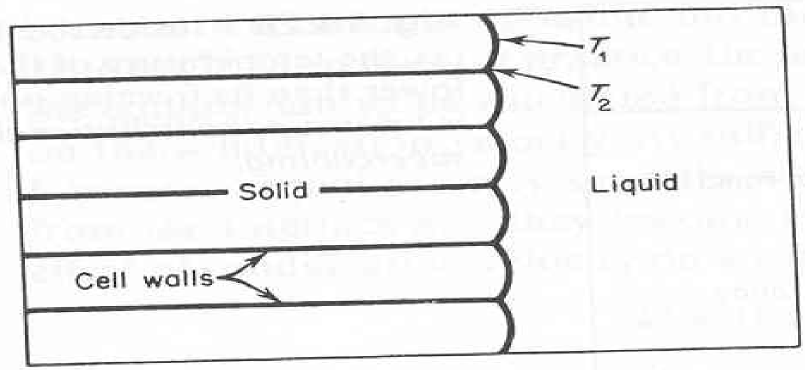
Freezing In Alloys



Part of an isomorphous binary phase diagram



A simple case of one-dimensional freezing, showing how composition changes as solidification proceeds from left to right.



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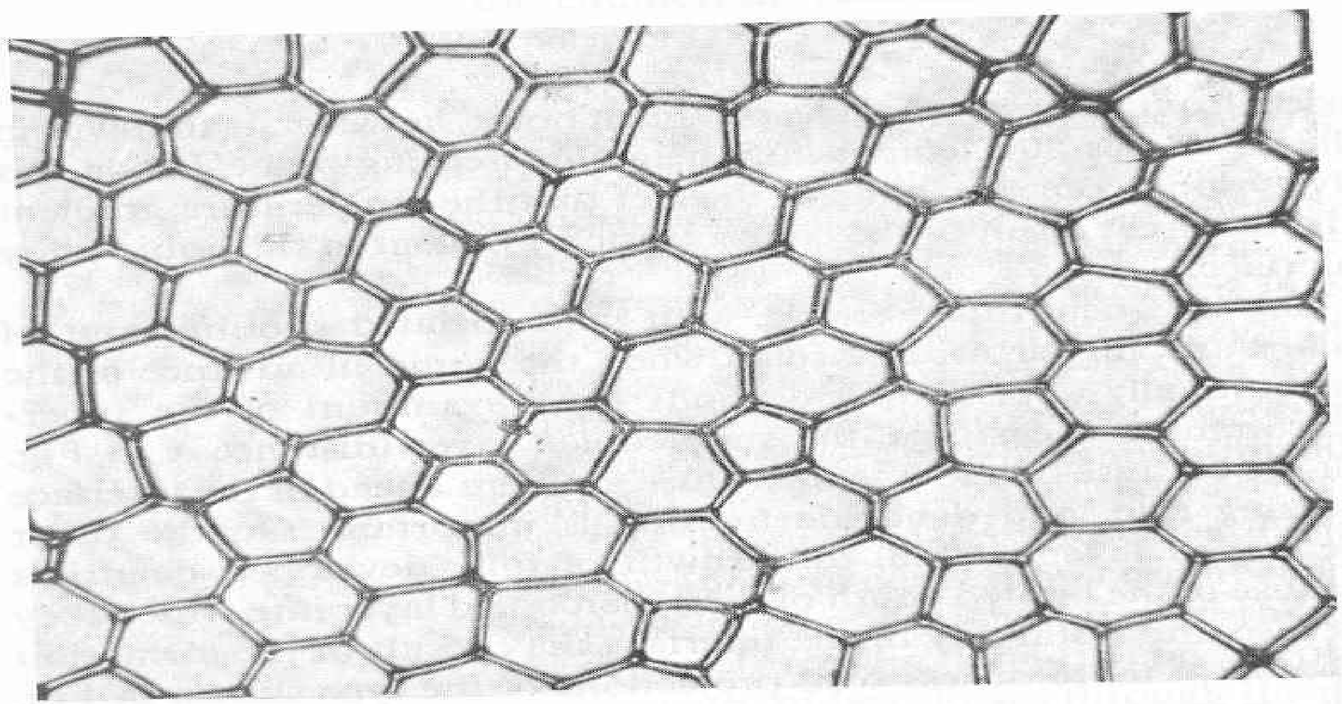


Freezing of Ingots

- Very important practical implications
- Much effort devoted to controlling this
- Plate, beams and sheet are worked from ingots to their final shape
- Several zones:
  - Chill zone—nucleation and growth
  - Columnar zone—dendritic growth
  - Central zone-- constitutional supercooling

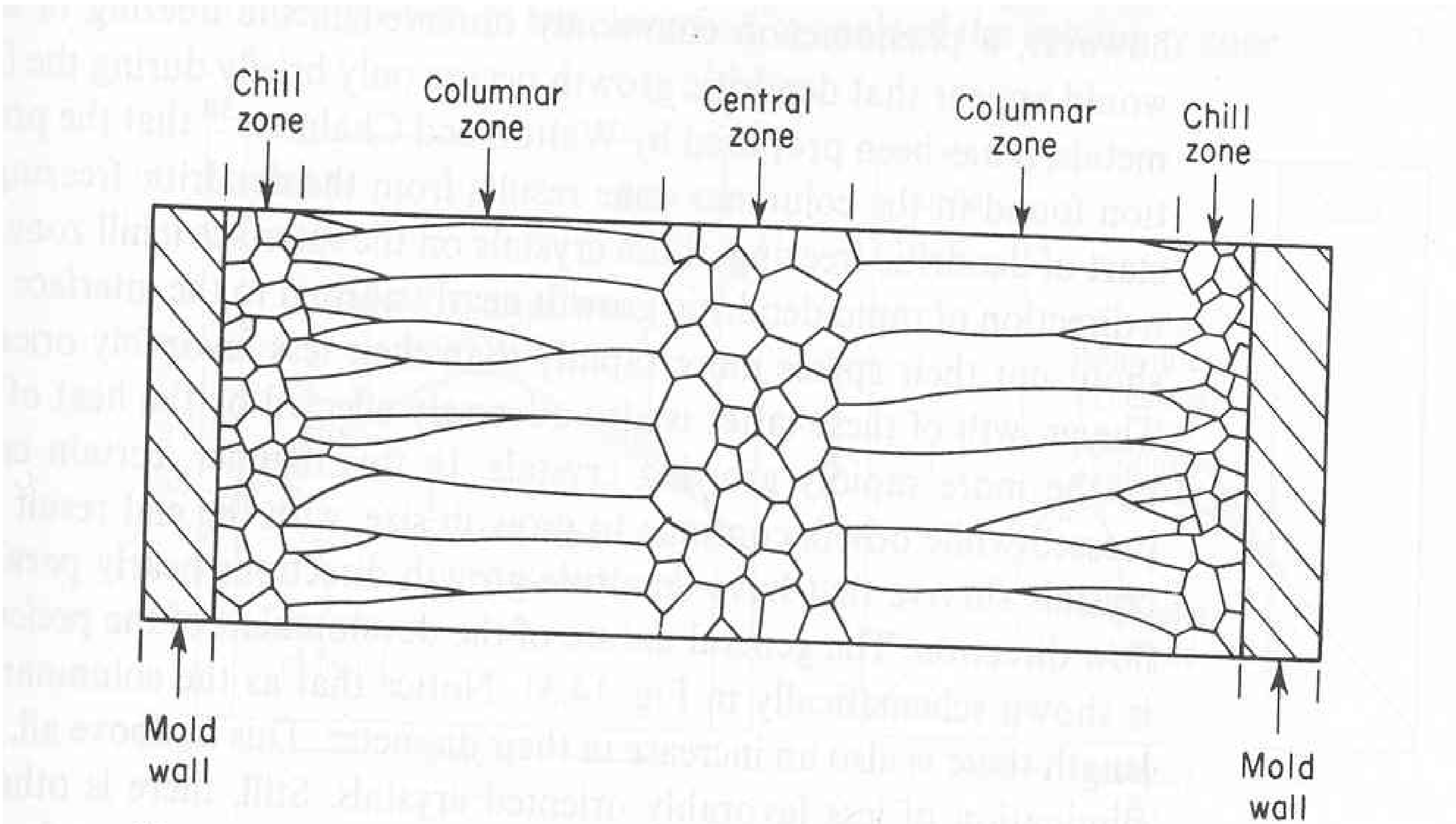


Fig. 14.31 A section through

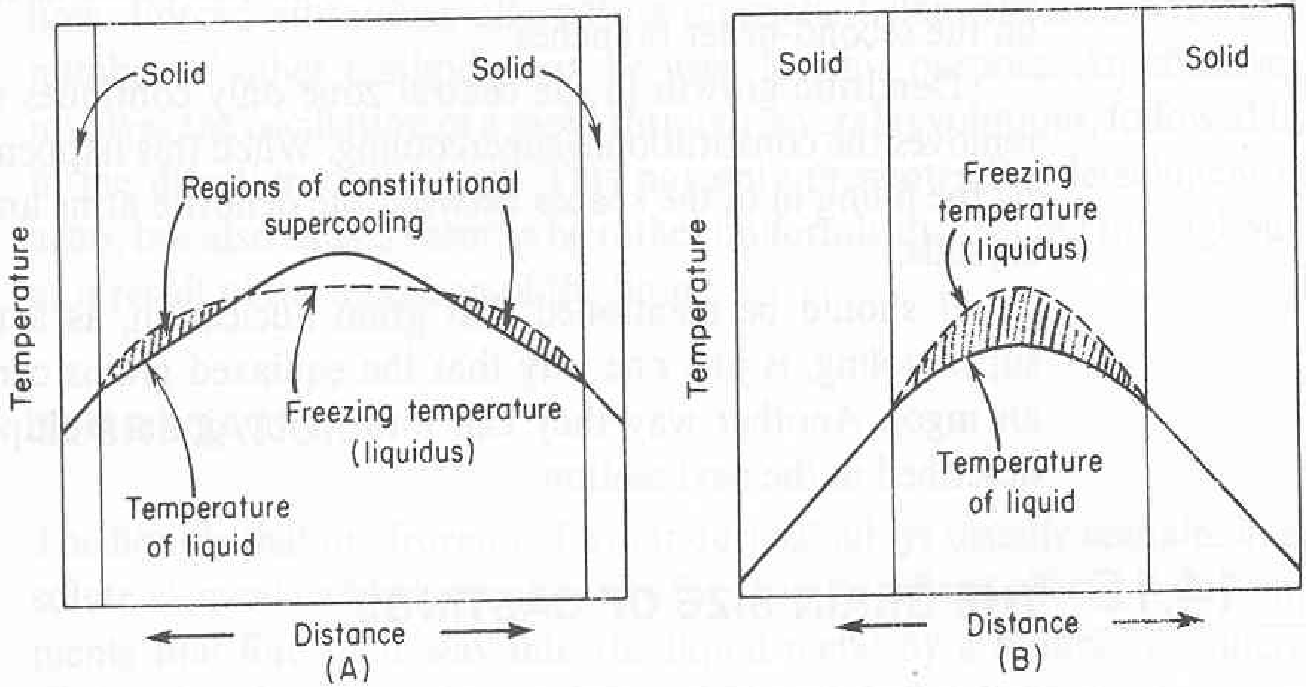
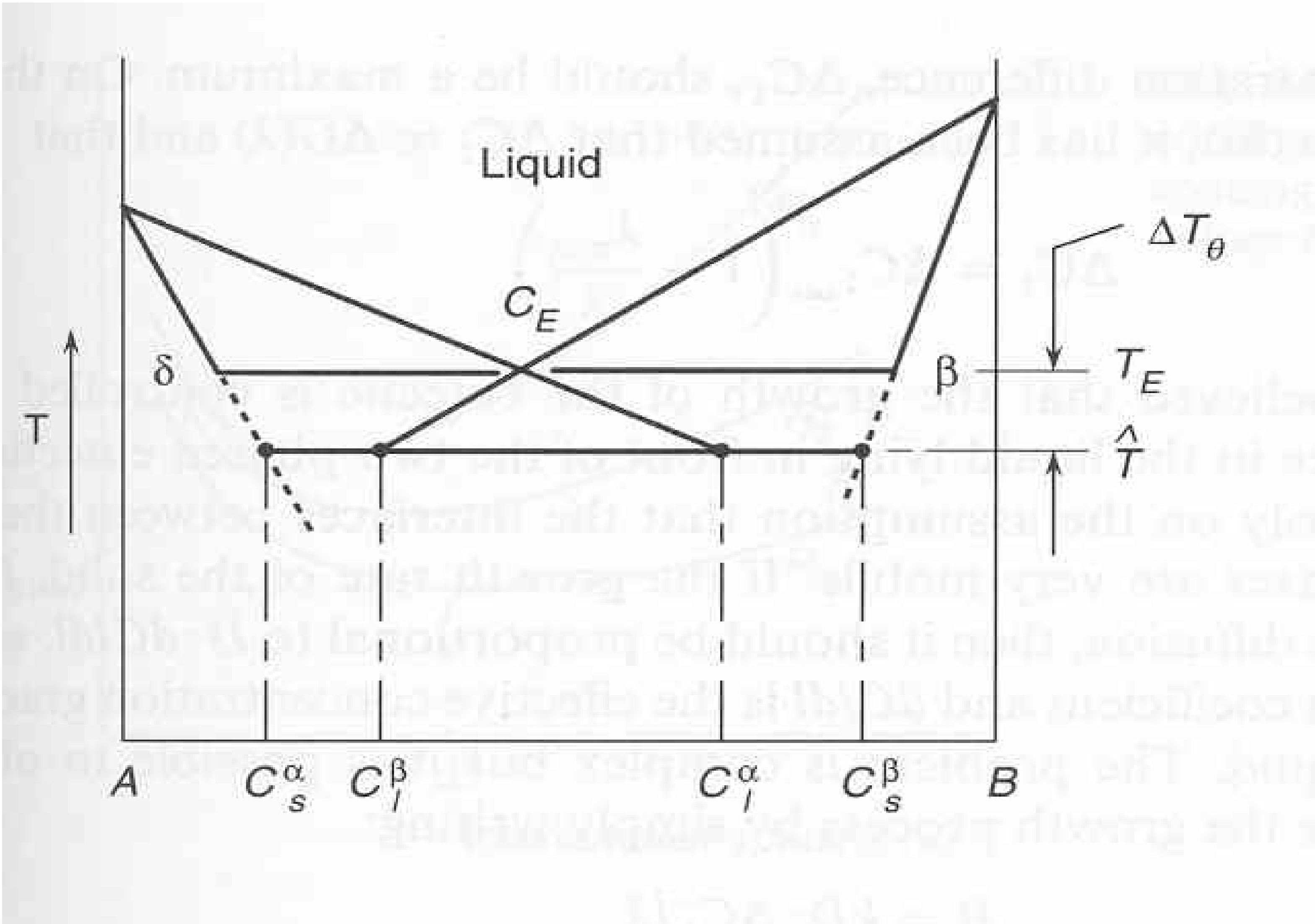


Fig. 14.32 The development of the constitutional supercooled region at the center of an alloy ingot that produces the central equiaxed zone of the ingot.

Eutectic Freezing

- Usually a coupled microstructure
  - Plates
  - Rods
- Growth is controlled by diffusion in the liquid ahead of the two phase solid
- Spacing can be based on the growth rate
- Very rapid solidification
  - Glass
  - Uniform distribution of particles


Liquid
ΔT_θ
C_E
δ
β
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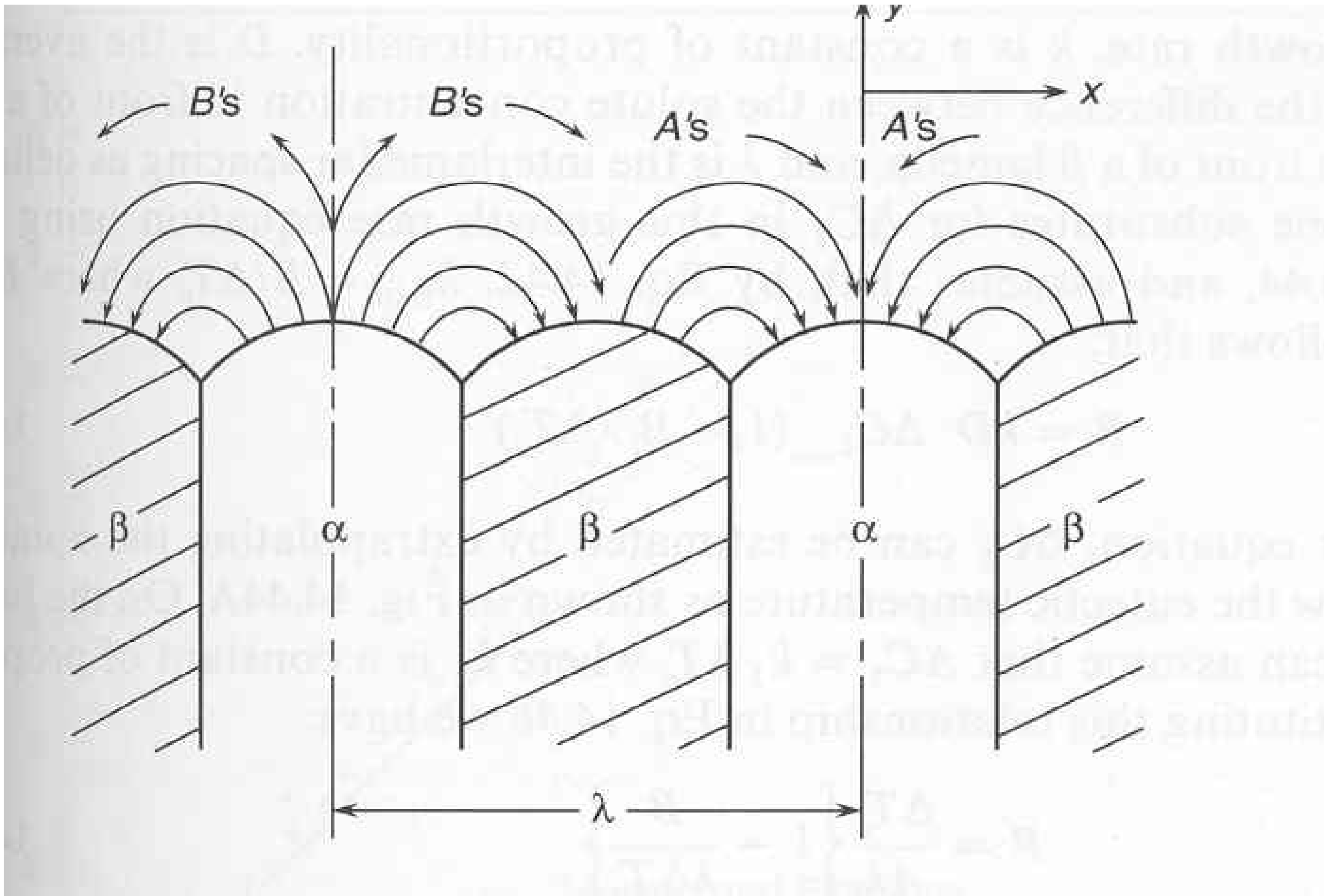
T
$\hat{T}$
A
C_s^α
C_l^β
C_l^α
C_s^β
B



y
x
B's
B's
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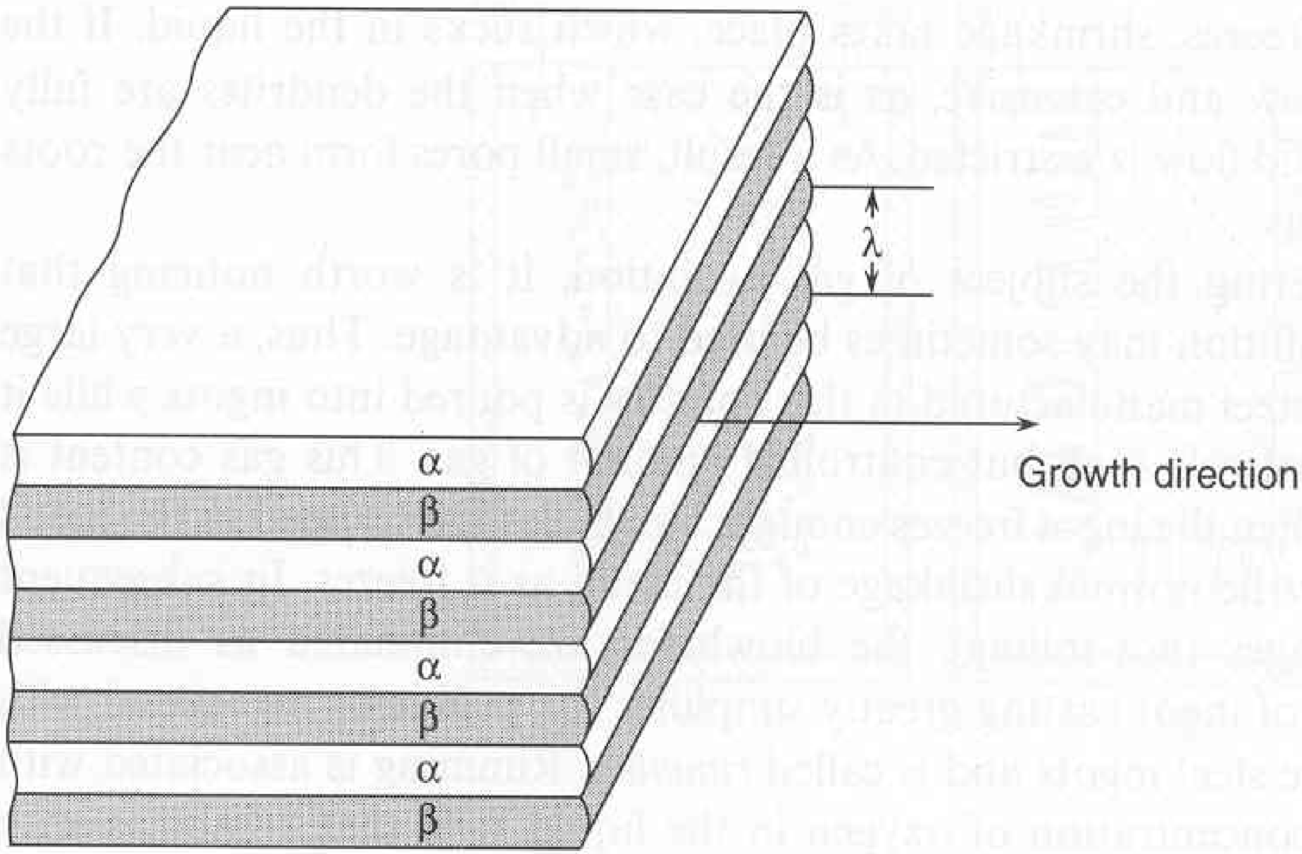
λ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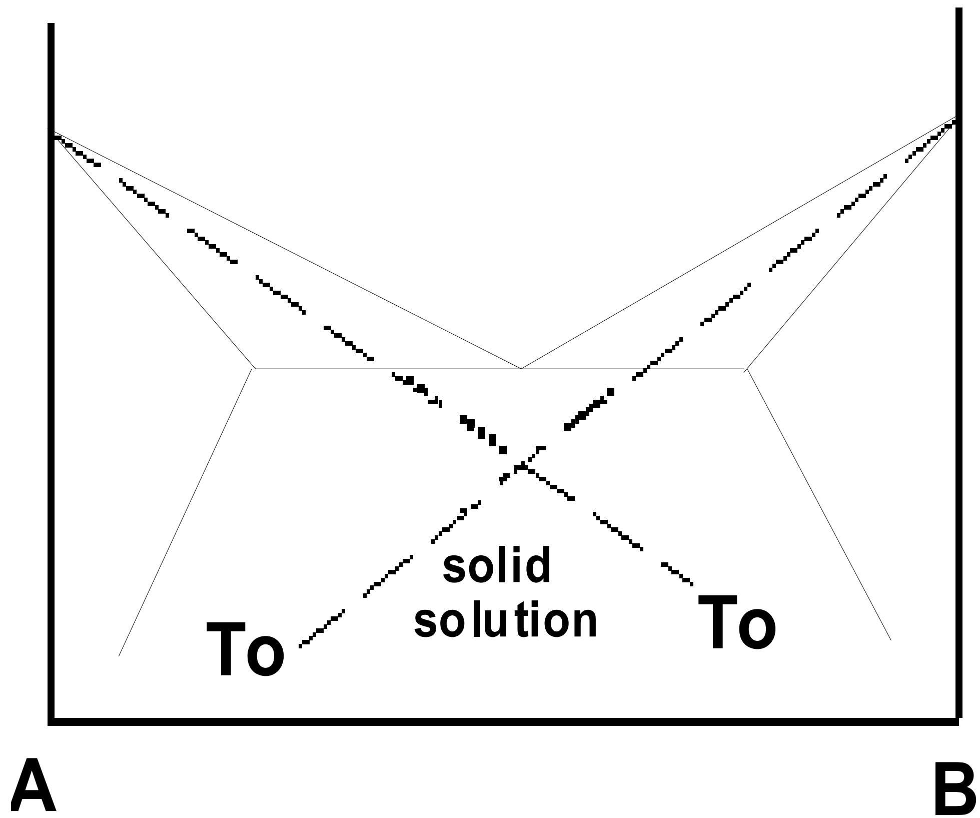
Growth direction

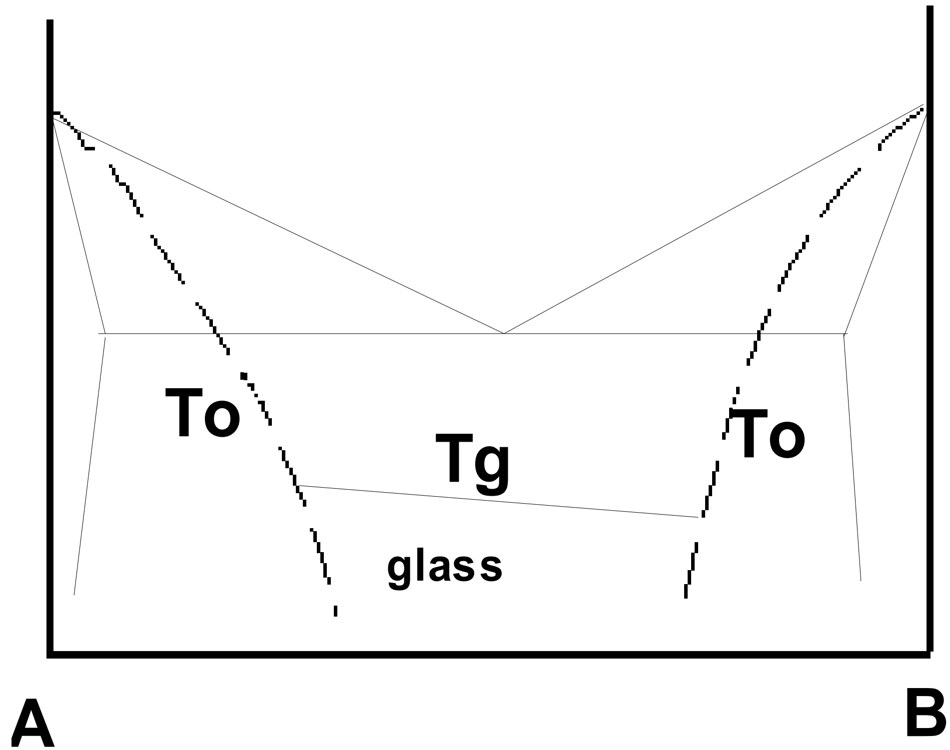
Metallic Glass

Metallic Glass (1)



Intersecting or continuous To curves give metastable solid solution

Metallic Glass (2)



Non-Intersecting To curves lead to the possibility of glass formation. Tg is the glass transition temperature.

Rapid cooling to a temperature below Tg, for compositions between the two To curves can result in the formation of a metallic glass.

Viscosity of the liquid increases rapidly as the temperature is lowered, and finally atomic movement is too slow to permit crystallization.

Metallic glass applications include transformer cores and golf clubs.

